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Investigation of Impurity Concentration
and Electrical Properties Near Interfaces

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Progress during the past year has been made in the following

areas:

1) Problems in the computer control system of the Quadrupole

SIMS instrument at USC have been resolved and it has been possible to

obtain SIMS depth profiles with this instrument. However, the primary

beam current densities have been too low to obtain depth profiles over

distances significantly greater than 1 μ in a reasonable period of time.

Because of this, it was considered desirable to utilize the facilities

at the University of Illinois to obtain SIMS data on the specimens of

GaAs:Cr that have been examined by cathodoluminescence and photoluminescence.

2) In a visit to the University of Illinois, January 18 and 19

depth profiles of 12 specimens were obtained using a CAMECA IMS-3F.

3) Further analysis of the cathodoluminescence data was made and

and important correlation was found between the 1.363 eV peak in the catho-

doluminescence spectra and the resistivity of the thermally-converted

layers.

4) After obtaining the SIMS results with the IMS-3F it was found

that some of the assumptions previously made concerning the results of

cathodoluminescence experiments were not valid. However new conclusions

could be drawn in view of these new data.

5) A draft of a paper combining the results of photoluminescence,

cathodoluminescence and SIMS has been prepared for submission to the

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The problem of thermal conversion in semi-insulating gallium arsenide was examined using cathodoluminescence, photo-luminescence and secondary ion mass spectrometry. The results indicated that a key role is played by the formation of $Si_{(as)}-V_{(ga)}$ complexes.

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Journal of Applied Physics and a shorter paper for presentation at the

EMSA/MAS conference in Washington, August 9-13 has been submitted.

Copies of these papers are attached.

During the remaining period of the grant it is planned to carry out

further SIMS investigations of the Cr depth distributions and to attempt

to understand the mechanism for Cr depletion in the converted layer.

Investigations will also be made to try to determine the Si concentrations

more accurately by using ion implanted specimens as standards.

Cathodoluminescence and SIMS Study of the Thermal Conversion of GaAs

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Cathodoluminescence has been used to study the conversion of semi-insulating GaAs to p-type as a result of different heat treatments. Low temperature cathodoluminescence and photoluminescence spectra are compared and differences are attributed to the difference in the excitation depth in these techniques. The cathodoluminescence spectra at 30°K indicate that the 1.23 eV emission band in the as-grown chromium-doped semi-insulating GaAs is associated with a $Si_{Ga}-V_{Ga}$ complex. Cathodoluminescence spectra of heat-treated material show emission bands at 1.363 eV, 1.407 eV and 1.496 eV which correspond to the acceptor levels introduced through the site transfer of silicon. The 1.363 eV peak intensity increases monotonically with increasing carrier concentration in the converted layer. Secondary ion mass spectrometry depth profiles show that this peak is not due to Cu and hence that it may be due to recombination involving a $Si_{As}-V_{Ga}$ complex.

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Introduction

Looking forward to the near future, gallium arsenide appears to be a promising material for high speed, high performance IC technologies now under development.[1] There are, however, several major problems associated with GaAs devices based on the use of semi-insulating substrates.[2] One of these problems results from the heating of semi-insulating GaAs under typical epitaxial growth conditions or post ion-implantation annealing; this frequently results in the semi-insulating GaAs substrates undergoing surface modification with the formation of a low resistivity surface layer. The low resistivity layer has been called a thermal conversion layer. This phenomenon was first reported by Edmond[3] and Wysocki.[4] Since then a variety of techniques such as photoluminescence,[5-16] cathodoluminescence,[17] electrical measurements,[10,11,18-21] photoelectric measurements,[19] Schottky barrier measurements,[22] SIMS,[23] AES,[16] DLTS,[24] and SEM[25] have been used to study this effect but the true causes of this effect are still somewhat ambiguous. Among these characterization techniques, the photoluminescence technique has been the most popular one. Photoluminescence spectra of thermally-converted layers sometimes show two emission bands at 1.36 eV or 1.41 eV. The origin of these two emission bands is controversial. The 1.41 eV emission band has been assigned by various investigations to recombination at a manganese acceptor on a Ga site[5,9,11,26,27] (Mn_{Ga}), recombination due to a shallow acceptor-arsenic vacancy complex[6,7,13,28-31] and recombination due to arsenic vacancies.[10,17,32] The 1.36 eV emission band has been assigned to recombination at a copper acceptor on a Ga site[6,33-36] (Cu_{Ga}^-), recombination at a shallow acceptor-gallium vacancy complex[18,28,37] and recombination at gallium vacancies.[15-16]

In the present work low-temperature cathodoluminescence and SIMS have
been used to study the nature of the thermal conversion phenomenon in GaAs.
Cathodoluminescence has the advantage (compared with photoluminescence)
that with readily available beam voltages (30-40 KeV) it is easy to get
a mean excitation depth in the specimen comparable to the thickness of
the thermal conversion layers ($\sim$1-2 μm). Hence, by using cathodoluminescence
it is possible to study the properties of the thermal conversion layer
at depths significantly larger than those studied by photoluminescence
(<<1 μm). In this paper cathodoluminescence spectra and photoluminescence
spectra are compared for one case of a thermally converted layer and results
from cathodoluminescence studies of 14 specimens of GaAs including 6 heat-
treated specimens are given. From the results obtained on specimens heat-
treated by two different techniques, and using the results of SIMS depth
profiles a model is proposed for the thermal conversion of GaAs.

Experimental Procedures

Chromium-doped semi-insulating GaAs wafers (100 orientation) from
Laser Diode Laboratories or Crystal Specialties, Inc. were heat treated
at the Naval Oceans Systems Center and at Hughes Research Laboratories.
Typical specimen preparation consisted of the following steps: a) mechanical-
chemical polishing b) ultrasonic cleaning using a sequence of electronic
grade solvents (trichloroethylene, acetone, methanol and dionized water)
and drying by a blast of nitrogen gas. Thermal annealing of the GaAs
samples was done by two different annealing techniques. In the first case
(specimens from NOSC) the annealing was done in a temperature-controlled
quarts tube furnace. They were placed on a graphite boat and exposed to
a continuous flow of palladium-diffused hydrogen. The specimens were
annealed at temperatures from 750°C to 900°C one for one hour, then the

furnace was turned off and the specimens removed after they cooled to ambient temperature. In the second case (specimens from Hughes Research Laboratories), the GaAs was annealed by using the melt-controlled ambient technique (MCAT).[38] In this technique a crucible which contains several kilograms of Ga saturated with GaAs was enclosed in an all-quartz annealing chamber which is connected to a stainless steel entry chamber through a high vacuum valve. The annealing chamber was continuously maintained in an ambient of palladium-diffused hydrogen. Samples to be annealed were held in a specially designed graphite holder, with a sliding cover. Annealing was performed by immersing the holder for two hours in a melt maintained at 800°C with the graphite cover closed so that the melt did not come in contact with the solid specimens.

The cathodoluminescence measurements were made using a clean-vacuum electron beam column that has been previously described by Marciniak and Wittry.[39] In order to get an excitation depth approximately equal to the thickness of thermal conversion layers, an accelerating voltage of 40 KV was used (at this voltage the electron range is about 6 μm in GaAs and the mean excitation depth is about 1.8 μm). The electron beam spot size was 10-15 μm and the typical beam currents were 0.25-10 nA. The samples' temperature was held at 30°K by using an open-cycle Joule-Thompson refrigerator. In spite of this low specimen temperature no contamination effects due to electron-beam irradiation were observed. The specimens were mounted on a copper block using indium and the specimen temperature was monitored by a copper-constantan thermocouple. The cathodoluminescence from the specimens was modulated by a 11 Hz mechanical chopper and focussed on the entrance slit of a plane grating spectrometer (Spex Industries, Inc.,

Model No. 1700-II) having a grating blazed for 7500 Å. A Corning 2-60

glass filter was used to discriminate the cathodoluminescence from the

native thin oxide layer on the surface of GaAs samples.[40] The detector

was an RCA C31034C photomultiplier which has a nearly-flat spectral response

from 3000 Å to 10300 Å. This detector was mounted in a thermo-electrically

cooled housing (Products for Research, Inc., Model TE-104 RF). The signal

was amplified and recorded by a synchronous amplifier (Brower Laboratories,

Inc., Synchronous Amplifier-recorder, Model 109).

For comparison with the cathodoluminescence spectra, photoluminescence

spectra were measured by W. Y. Lum of the Naval Electronics Laboratory Center

using either 6328 Å radiation from a 5 mW He-Ne laser or 6471 Å radiation

from a 500 mW Krypton laser. The focused beam at the specimen had a

cross section of 1 mm^2 and the emitted radiation was modulated by a mechanical

chopper at 100-200 Hz and focused the entrance slit of a Spex 1701 plane

grating spectrometer of 0.75 m focal length. The grating was blazed at

1.6 µm and the detector was a cooled photomultiplier with S-1 response.

Electrical measurements were made at Hughes Research Laboratories

by C. L. Andersen and at NOSC by W. Y. Lum. Square ($\sim$4 mm x 4 mm) Hall

specimen, were cut from the wafer. Hall and conductivity measurements

using the Vander Pauw configuration were used to determine the carrier

concentration and mobility.

SIMS depth profiles were obtained using a Cameca IMS-3F and an

Applied Research Laboratories prototype QMAS. With the IMS-3F, typically

a 250 µ x 250 µm area was raster-scanned with a 9.55 KeV positive oxygen

beam of 2-3 µA and the central area of 150µ in diameter was focused on

the entrance slit of the mass spectrometer. For the QMAS instrument

a 500 x 500 µ area was raster-scanned and the central area 250 ·x 250 µm

area was selected with an electronic aperture. A positive oxygen beam

of $\sim$.5-1 µA at 10 kV was used. In both instruments charging of the semi-

insulating specimens was an important problem. This was minimized in both instruments by using photoconductivity due to light from the illuminator for the sample viewing system. In the case of the QMAS, additional reduction of surface charging effects was obtained by a computer program that adjusted the specimen potential to maximize the intensity for a reference ion, typically $^{71}Ga^{+}$. The relative intensities of various ion species obtained from the two SIMS instruments were not the same. This is expected from the difference in "sensitivity factors" for the quadrupole vs the magnetic spectrometer instruments, and will be discussed elsewhere. To avoid confusion, only data from the IMS-3F are included in this paper.

Experimental results and discussion

In the initial phase of this investigation a major concern was the lack of agreement between the photoluminescence and cathodoluminescence spectra for a given specimen. Figure 1 shows a comparison of the photoluminescence spectrum at 4°K and the cathodoluminescence spectrum at 30°K for specimen T2. In order to investigate this discrepancy photoluminescence spectra were recorded at various temperatures and cathodoluminescence spectra were recorded at various beam current densities, various temperatures and at two different electron beam voltages. The results of these studies indicated that the difference in the CL and PL spectra was not due to a difference in injection level or specimen temperature but due to a difference in the depth of the region which is being sampled by these two techniques. For the visible light used in photoluminescence the absorption coefficient of GaAs is $\sim 3.6 \times 10^{4}$ cm^{-1} and the penetration depth (1/e distance) is $\sim$.28 μm. The 40 keV beam, on the other hand, generates carriers to a depth of 5-6 μm. In order to elucidate this point, the depth distribution of excess carriers was calculated for a reduced surface

recombination velocity of 50 and a carrier diffusion length of 0.76 μm using a Gaussian approximation for the excess carrier generation as previously described by Kyser and Wittry.[41] The results shown in Fig. 2 clearly indicate the difference in sampling depth for optical and electron beam excitation. However, it should be noted that the excess carrier distribution will be different from the distributions shown if there are gradients in the concentration of electrically-active impurities or defects (this may give rise to electric fields and hence drift of carriers as well as diffusion of carriers). It should also be noted that the diffusion length of excess carriers in the converted layer will decrease with increasing carrier concentration and hence the sampling depth (particularly for photoluminescence) will be different for different specimens. Specimen no. T2 represents an extreme case because of its very high carrier concentration (refer to Fig. 6).

The results of the cathodoluminescence spectra and electrical measurements on the 14 specimens studied are summarized in Table I. Typical cathodoluminescence spectra are shown in Figures 3 and 4. Figure 3 shows the cathodoluminescence spectra at 30°K for specimens T1 and T2 corresponding to before (dashed line) and after (solid line) annealing in H_2 at 800° for 1/2 hour. Both samples show a narrow peak at 1.509 eV (8215 Å), about 6 meV lower than the band gap for those temperatures.[41] This energy corresponds closely to that of a simple hydrogenic donor impurity[43] and is assumed to result from recombination involving silicon on a gallium site (Si_{Ga}) and the valence band. The unheated specimen (T1) shows a small peak at 1.23 eV (10088 Å). This peak was attributed earlier by Hwang[7] and Williams[42] to recombination involving a Si donor-Ga vacancy complex ($Si_{Ga}-V_{Ga}$). This 1.23 eV peak can always be found in Si doped n-type GaAs.[7,37,44] Thus for the unannealed Cr-doped semi-insulating GaAs the presence this 1.23 eV peak means that

this sample contains silicon as an impurity. The heat-treated specimen
(T2) shows a small peak at 1.496 eV (8289 Å); this is considered to be
a free-to-bound transition produced by a free electron captured at a
neutral acceptor site. The shallow acceptor may be C_{As}[8,45] which was
introduced into crystal during the annealing process because the GaAs
sample was put on a graphite boat. Two additional peaks at 1.407 eV
(8816 Å) and 1.363 eV (9100 Å) and two shoulders at 1.33 eV (9320 Å)
and 1.296 eV (9570 Å) are also evident in this figure. The 1.407 eV
peak is presumed to be a Si acceptor-arsenic vacancy complex (Si_{As}-V_{As})
which was reported previously in doped samples of bulk GaAs.[46] The
1.363 eV peak is an important key to understanding the mechanism of
thermal conversion and will be discussed further in the following
paragraphs. The two shoulders at 1.33 eV and 1.296 eV are LO-phonon
replicas of 1.363 eV peak.

Figure 4 shows the cathodoluminescence of specimens T9 and T10
corresponding to before (dashed line) and after (solid line) annealing
at 800°C for 2 hours using the melt-controlled ambient technique. It
will be noted that the unheated specimen (T9) shows the same strong
peak at 1.23 eV as in Fig. 3 and that this peak also disappears on
heat treatment. The heat-treated specimen (T10) also shows the peaks
at 1.407 eV and 1.363 eV which were obtained from T2.

In the course of this work, the temperature dependence of the peak
position was also measured. The results are shown in Figure 5. For
comparison the temperature dependence of the bandgap is shown (line a)
as previously reported by Casey and Panish.[47] It can be noted that the
1.363 eV peak has the same temperature dependence as the bandgap while
the 1.509 eV peak has a slightly different temperature dependence.

Figure 6 indicates a strong correlation of the intensity of the 1.363 eV peak with carrier concentration in the converted layers. This peak was not seen in the photoluminescence spectra for specimen T2; if it is present it was apparently masked by the LO phonon replica of the 1.41 eV peak (8790 Å) as can be seen from Figure 1. The high intensity of the 1.41 eV peak in the photoluminescence spectra and its lower intensity (relative to the 1.363 eV peak) in the cathodoluminescence spectra can be explained if it is assumed that the 1.363 eV peak involves a defect at a larger depth in the specimen than the 1.41 eV peak. This would be consistent with the assignment of the 1.41 eV to recombination involving an As vacancy and the 1.36 eV peak to recombination involving a Ga vacancy since it is expected that the As vacancy concentration will be very high at the surface and drop off sharply with distance due to the small self diffusion coefficient of As in GaAs. On the other hand the Ga vacancies will have lower concentration at the surface but will extend to larger depths because of a larger self diffusion coefficient. This possibility is indicated by a calculation of the vacancy concentration distribution of Ga and As based on results published by Chiang and Pearson[48] and shown in Figure 7.

Figures 8-10 show SIMS depth profiles for specimens T2, T10 and T14. Several important observations can be made from these results if we assume the concentration of each element is directly proportional to the ion intensity obtained from that element. First it will be noted that there is a strong depletion of chromium in a surface layer for all three specimens and the chromium concentration is about the same for specimens T2 and T10 but is higher in T14. Second, it will be noted that concentration of copper is not abnormally high in T2 compared to T10 and T14 (i.e. at most a factor of 3 compared to T10 and a factor of

~7 compared to T14.) Third, there is a tendency for the concentration of manganese to increase in the surface layer for T14 and T2 but the concentration of Mn in T2 does not exceed that in T10 by more than a factor of 10. Finally, the concentration of Si is high in all three of these heat-treated specimens and in fact is about the same in the unheated specimens.

If we assume that the intensity of the 1.363 eV peak is directly proportional to the concentration of the impurity or defect which is responsible for this transition then it appears that recombination due to Cu contamination is not responsible for this peak. Using a similar assumption regarding the 1.41 eV peak, it is possible to rule out Mn as being principally responsible for the 1.41 eV peak. Also, using an LTE model[49] for quantitative SIMS it is expected that silicon will be detected with a significantly lower sensitivity than Cr (approximately by a factor of 0.115 if the LTE temperature is 10,000°K or 0.0527 if the LTE temperature is 5,000°K. On this basis it seems that the Si concentration may be two to ten times higher than the Cr concentration in some of the specimens examined (T1, T2, T9 and T10). While it is possible that other ion species may interfere with the ^{28}Si peak, it seems unlikely that the intensities of these species e.g. ($^{14}N_2^+$, $^{12}C^{16}O^+$, $^{27}AlH^+$, $^{12}C_2H_4^+$, $^{56}Fe^{++}$, etc.) will be sufficiently high to account for the high intensity of the 28 AMU peak. On the other hand, if the Si concentration exceeds the Cr concentration, then in order to explain the semi-insulating nature of the bulk material it must be assumed that a significant fraction of the Si is electrically inactive. This could result from Si_{Ga}-Si_{As} pairing or SiO_2 microprecipitates. Further needs to be done concerning quantitative determination of Cr, Si and O in semi-insulating GaAs in order to understand some of the present SIMS results.

Summary and Conclusions

In the present work, we have clarified some of the ambiguities concerning thermal conversion of GaAs. Our work indicates that the 1.407 eV emission peak is probably due to a $Si_{As}-V_{As}$ complex and not to recombination at Mn impurities. It also indicates that the 1.363 eV peak is due to recombination involving a $Si_{As}-V_{Ga}$ complex and not to Cu contamination. Figure 11 summarizes the assignments of various radiative transitions observed in the present work. The tendency for thermal conversion is enhanced by the depletion of Cr in the thermally converted layer but this depletion alone cannot account for the thermal conversion. On the basis of the present results, the formation of a $Si_{As}-V_{Ga}$ complex appears to play a key role. Further work is required to determine the role of oxygen in this process. This may be done by SIMS using $^{18}O^{+}$ as a primary beam but will require the use of a SIMS instrument with mass filtering of the primary beam and low background of $^{18}H_2O$.

Acknowledgements

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Figure Captions

1 Comparison of cathodoluminescence spectrum at 30°K (dashed lines) and photoluminescence spectrum at 4.2°K (solid lines) for a specimen of GaAs:Cr heat-treated in H_2 for 1/2 hr at 800°C (specimen no. T2).

2 Comparison of the excitation vs depth and the resulting equilibrium carrier densities for photon excitation (solid lines) and electron beam excitation (dashed lines). The parameters used for electron beam excitation were V_{acc} = 40 KV, z_o = 0.65 μm, L = 0.76 μm, D_p = 3 cm^2/sec, J = 2A/cm^2 and <ε> = 5.35 eV. For optical excitation the parameters used were $α$ = 4 $μm^{-1}$ G_{op} = 10^{27}/cm^3 sec at the surface (L and <ε> had the same values).

3 Cathodoluminescence spectra at 30°K of specimen T1 (before heat-treatment: dashed line) and specimen T2 at 30°K (after heat-treatment: solid line).

4 Cathodoluminescence spectra at 30°K of specimen T9 at 30°K (before heat-treatment: dashed line) and specimen T10 (after heat-treatment: solid line). .

5 Temperature dependence of (a) GaAs bandgap (b) emission peak at 1.509, (c) emission peak at 1.407 eV (d) emission peak at 1.363 eV.

6 Relation between the cathodoluminescence intensity of the 1.363 eV peak (normalized to the 1.509 eV peak) and hole concentration.

7 Depth distribution of As and Ga vacancies for a specimen of GaAs heat treated at 800°C for 2 hr in H_2 (low Ga and As overpressures).

8 Logarithmic plot of ion intensities for ^{52}Cr, ^{28}Si, ^{12}C, ^{55}Mn and ^{63}Cu vs depth for specimen no. T2.

9 Logarithmic plot of ion intensities for ^{52}Cr, ^{28}Si, ^{12}C, ^{55}Mn and ^{63}Cu vs depth for specimen no. T10.

10 Logarithmic plot of ion intensities for ^{52}Cr, ^{28}Si, ^{12}C, ^{55}Mn and ^{63}Cu vs depth for specimen no. T14.

11 Emission lines observed in the present work and assignment of
    their most probable origin. Bands observed before annealing are
    a and d and bands observed after annealing are a - f.

Sample No.	Heat Treatment	Emission Peak (Å)	Peak (eV)	Ratio of 1.25 & 1.363 eV peak to 1.599 eV peak	Ratio of 1.363 eV peak to 1.25 eV peak	Carrier concentration p (cm^{-3})	Resistivity ρ (Ω-cm)
T1[a]	none	10000	1.25	1.26×10^{-4}	1		
T2[a]	800°C-1/2 hr.[c]	9100	1.363	9.2×10^{-2}	730.16	1.75×10^{17}	0.157
T3[b]	none	10000	1.25	2.4×10^{-4}	1		
T4[b]	750°C-1 hr.[c]	9100	1.363	7.7×10^{-3}	32	n.a.	n.a.
T5[b]	900°C-1 hr.[c]	9100	1.363	1.38×10^{-3}		n.a.	n.a.
T6[b]	900°C-1 hr.[c]	9100	1.363	2.1×10^{-4}		n.a.	n.a.
T7[b]	none	10000	1.25	1.34×10^{-4}	1		
T8[b]	800°C-1 hrs.[d]	9100	1.363	1.38×10^{-4}	1.03	3.015×10^{15}	50.89
T9[b]	none	10000	1.25	1.3×10^{-4}	1		
T10[b]	800°C-2 hrs.[d]	9100	1.363	2.1×10^{-4}	1.62	3.783×10^{15}	20.56
T11[a]	none	10000	1.25	1.6×10^{-4}	1		
T12[a]	800°C-2 hrs.[d]	9100	1.363	2.8×10^{-4}	1.75	4.716×10^{15}	17.17
T13[b]	none	10000	1.25	5.6×10^{-4}	1		
T14[b]	800°C-2 hrs.[d]	10000	1.363	1.8×10^{-4}			
		9100	1.363	1.2×10^{-3}	2.14	1.081×10^{16}	16.9

a: (100) oriented Cr-doped semi-insulating GaAs obtained from Crystal Specialties Inc.
b: (100) oriented Cr-doped semi-insulating GaAs obtained from Laser Diode Laboratories
c: Heat treatment in hydrogen using a tube furnace
d: Heat treatment using the melt-controlled ambient technique

Table 1 Summary of the specimens investigated and the important cathodolumi-
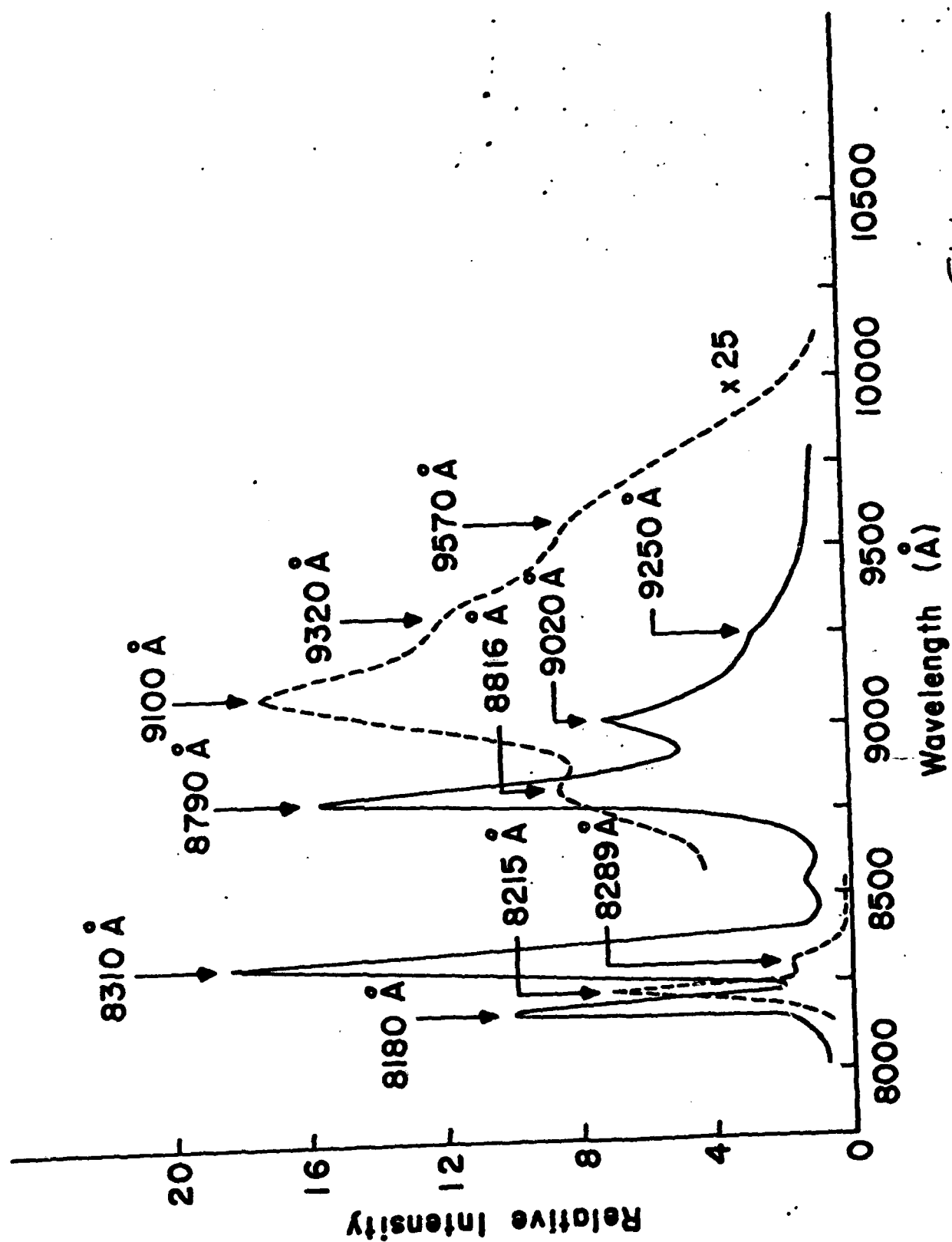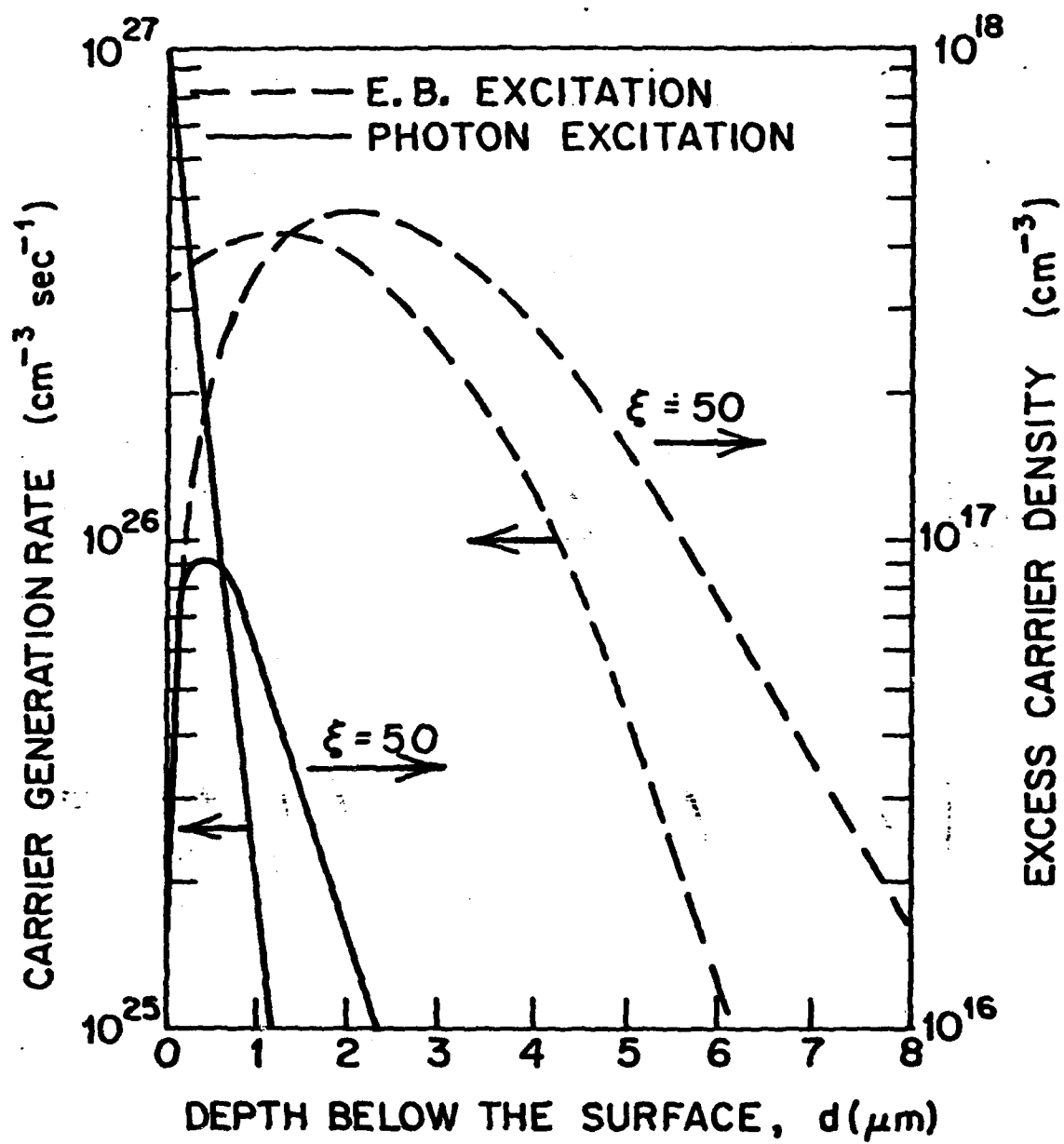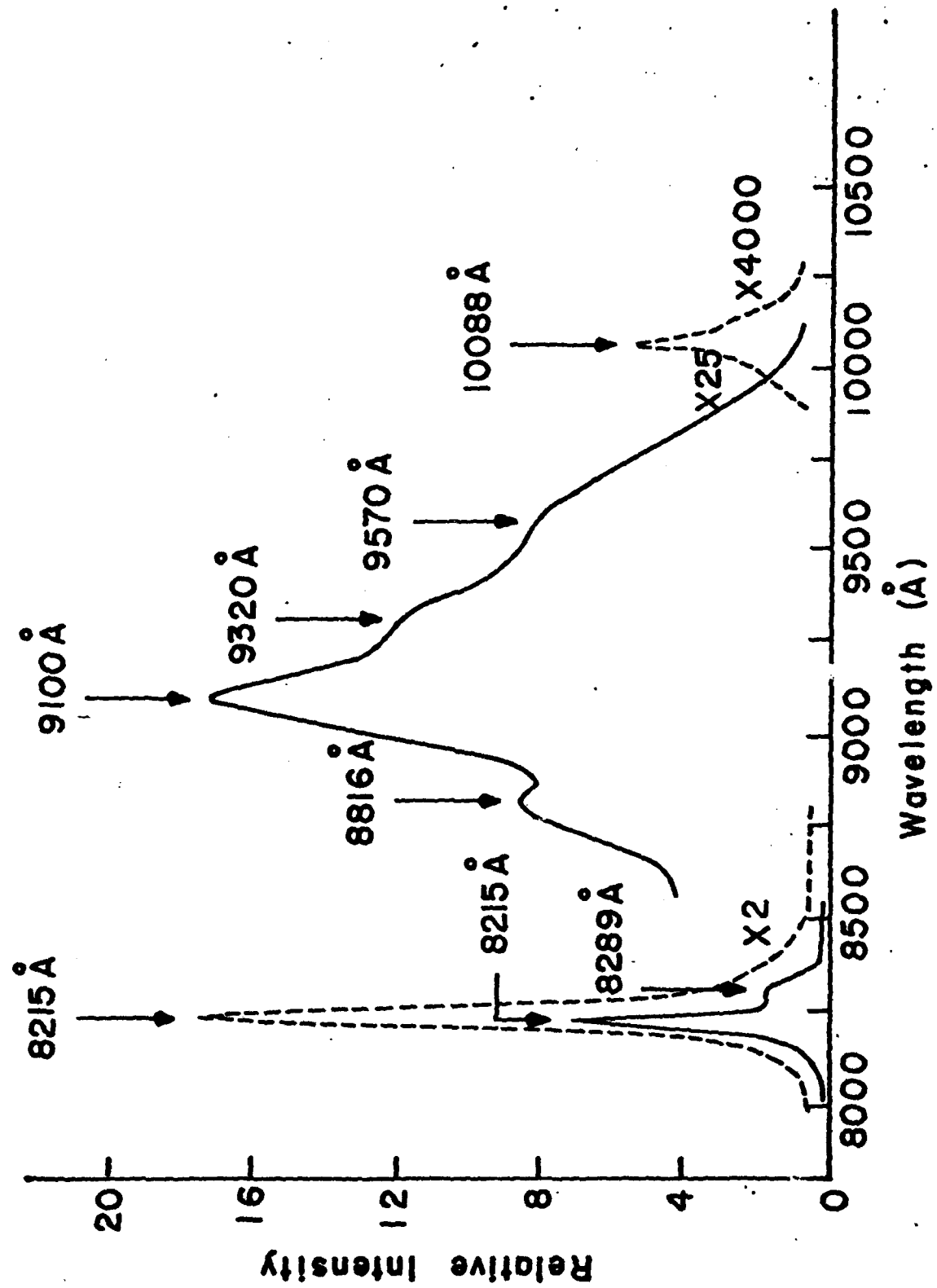nescence and Van der Pauw type Hall measurement results

Fig 1

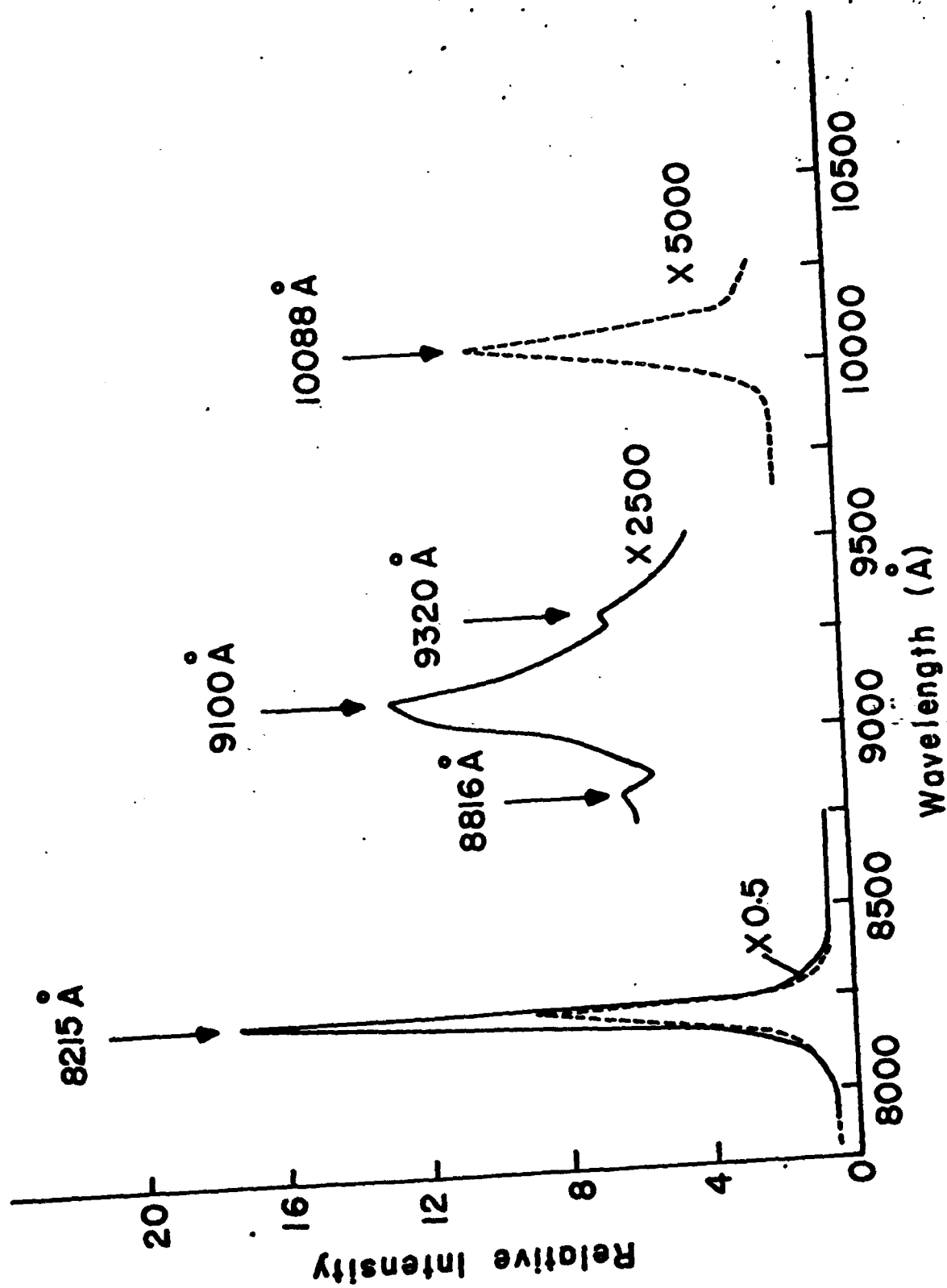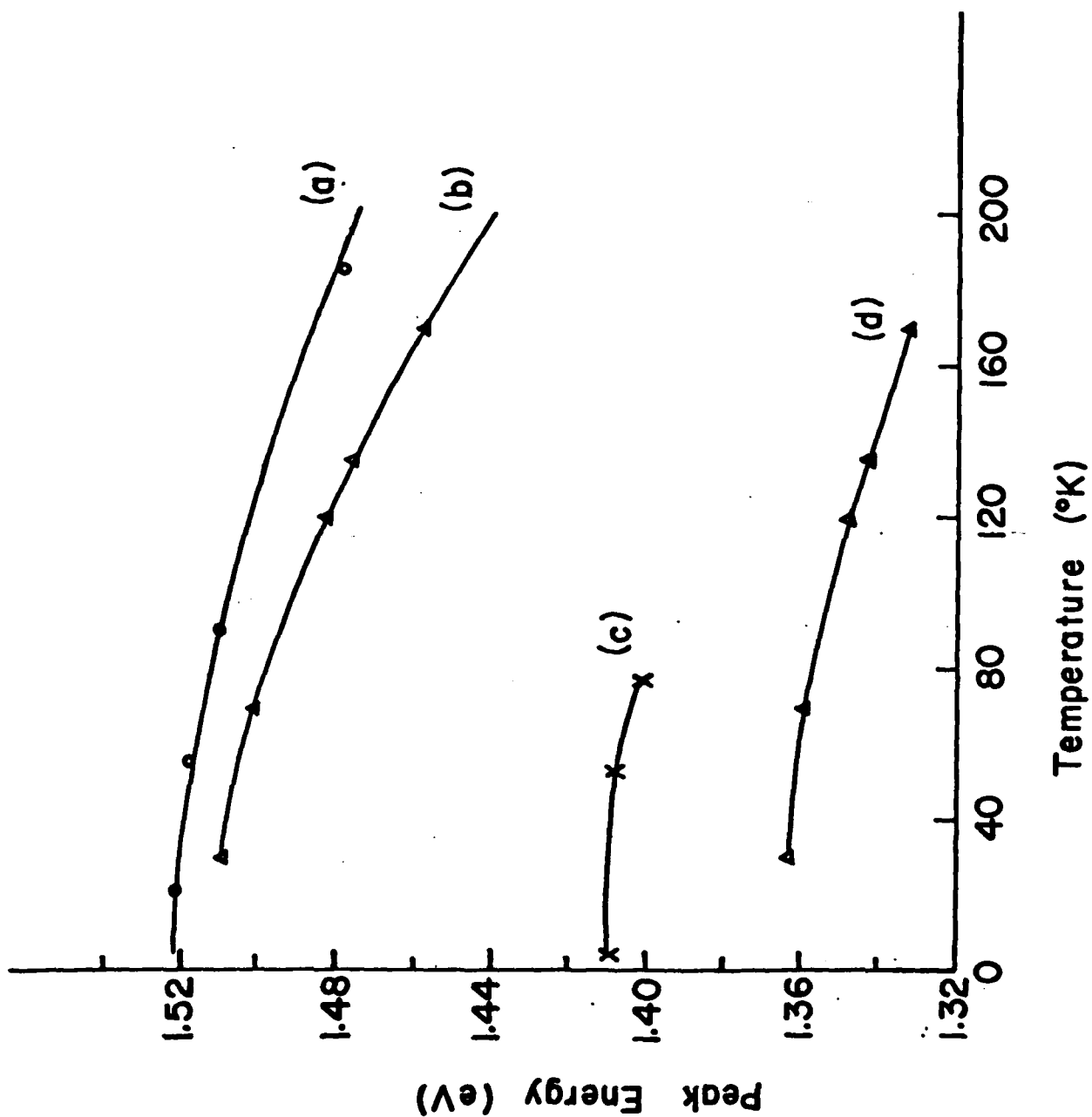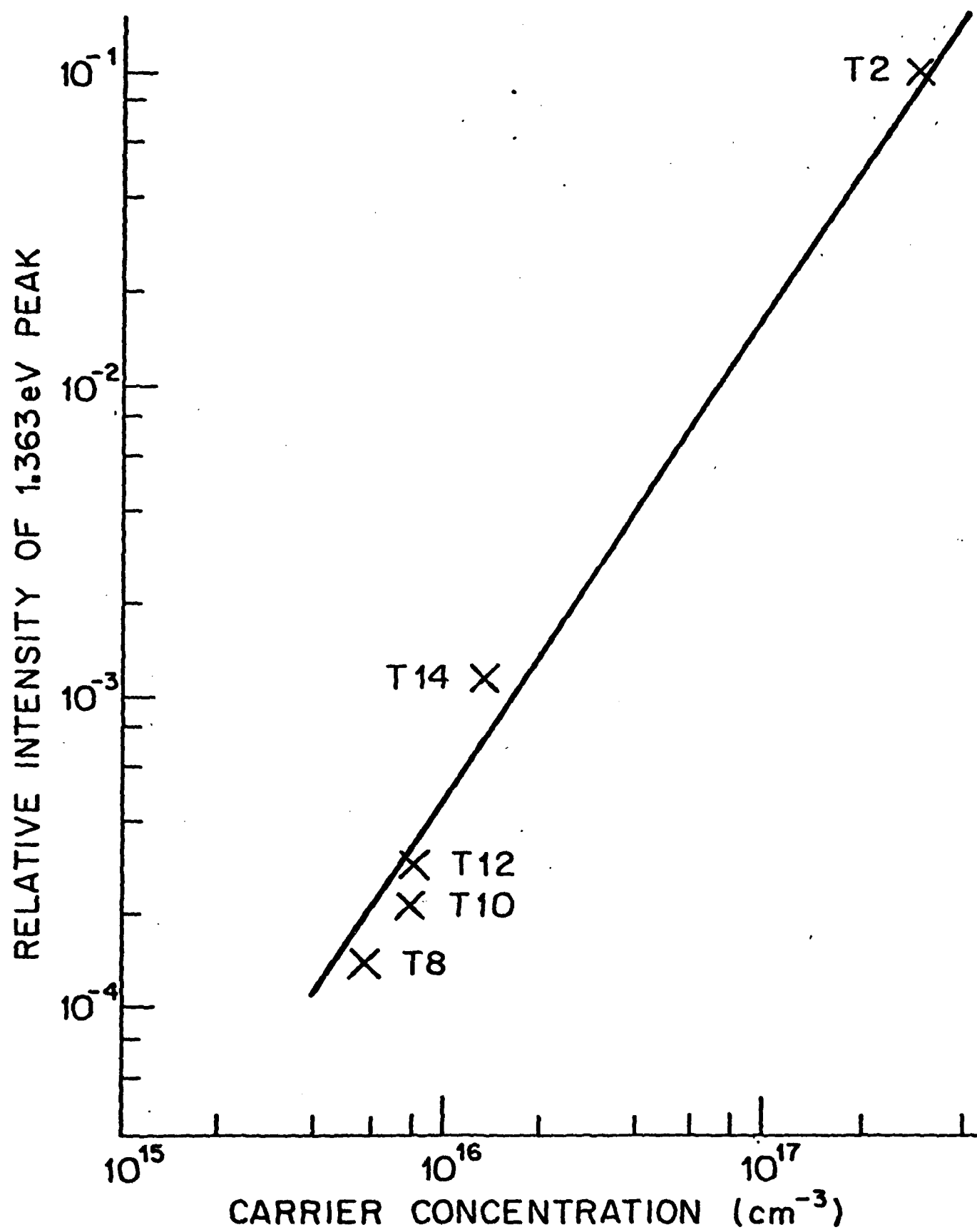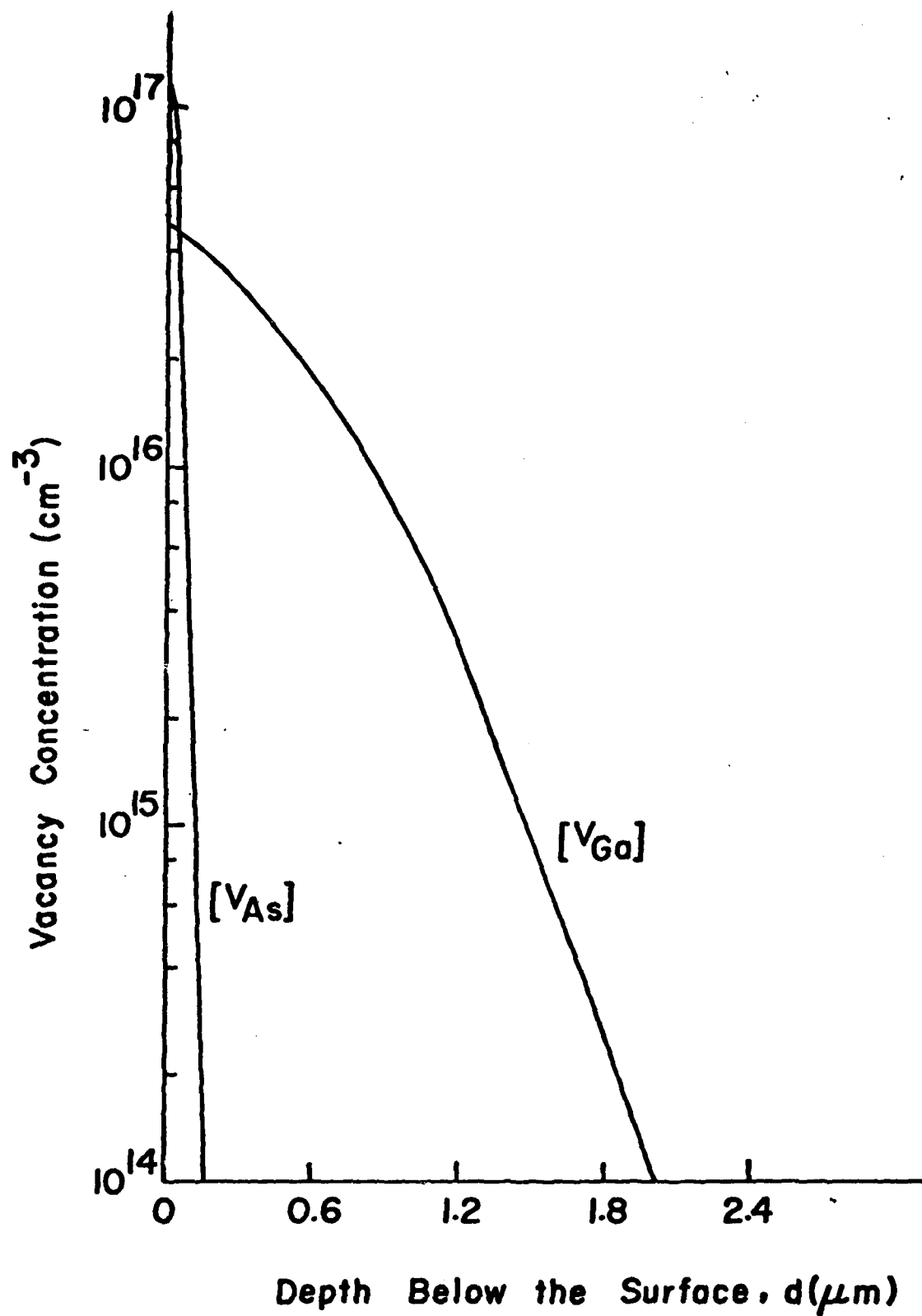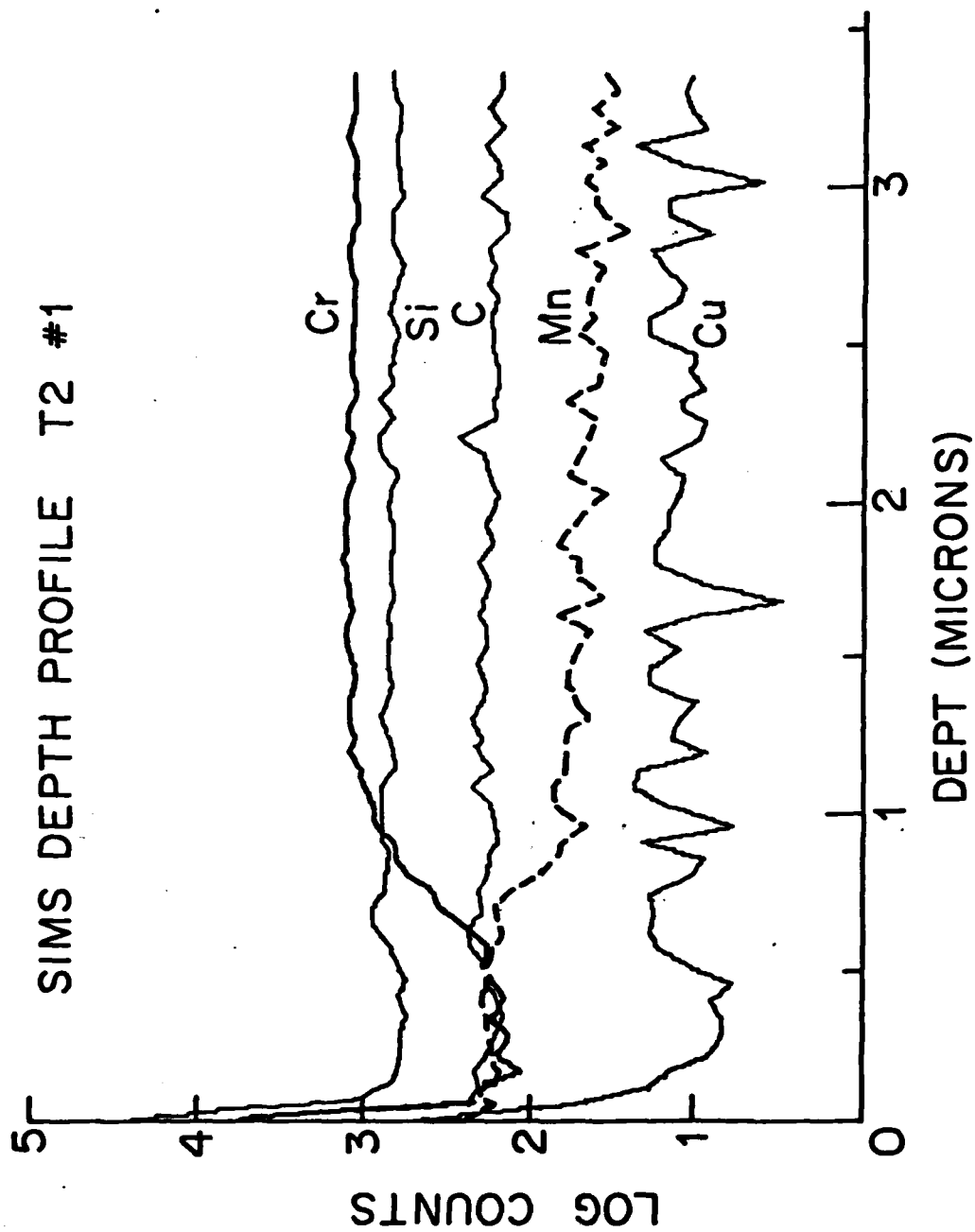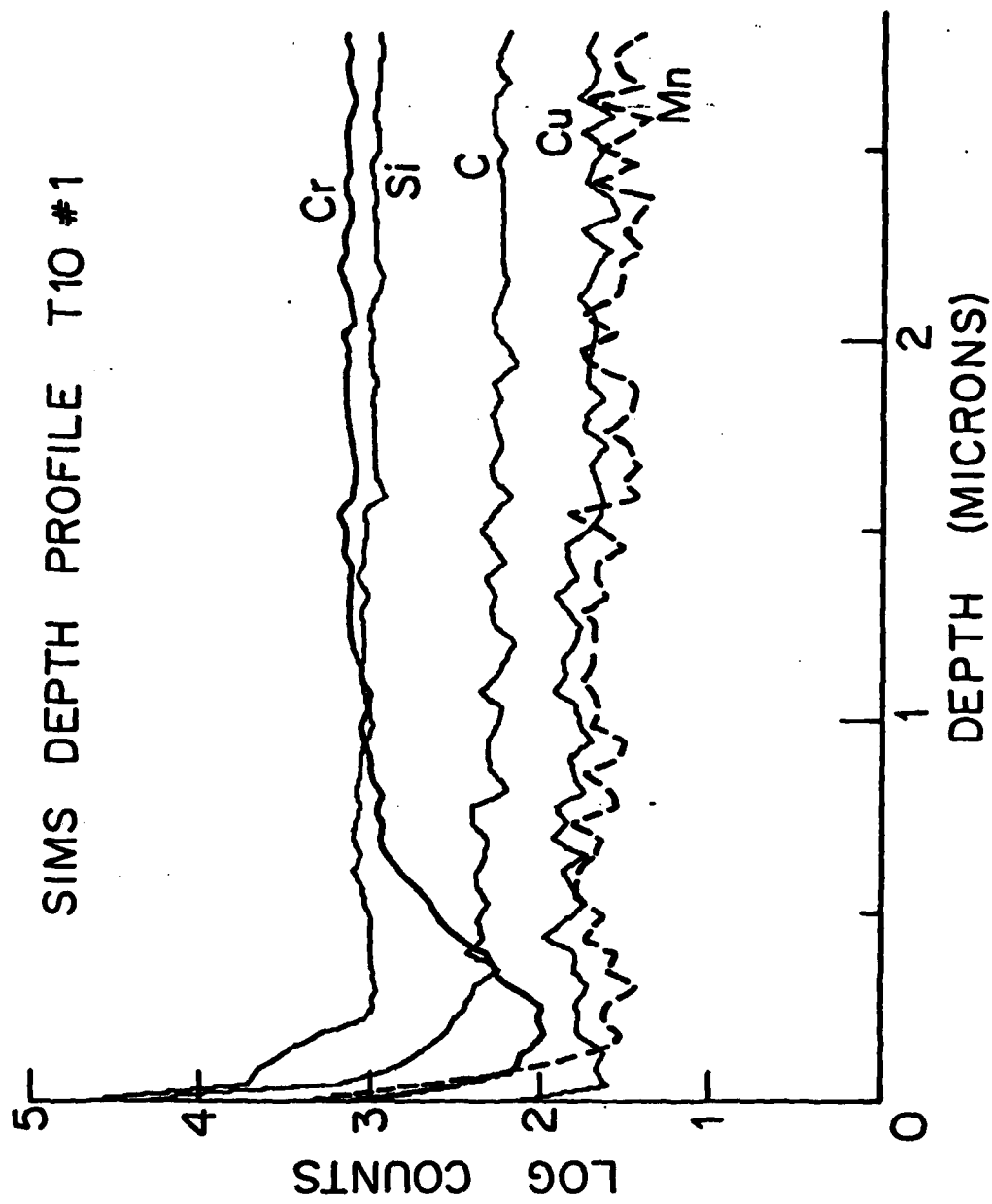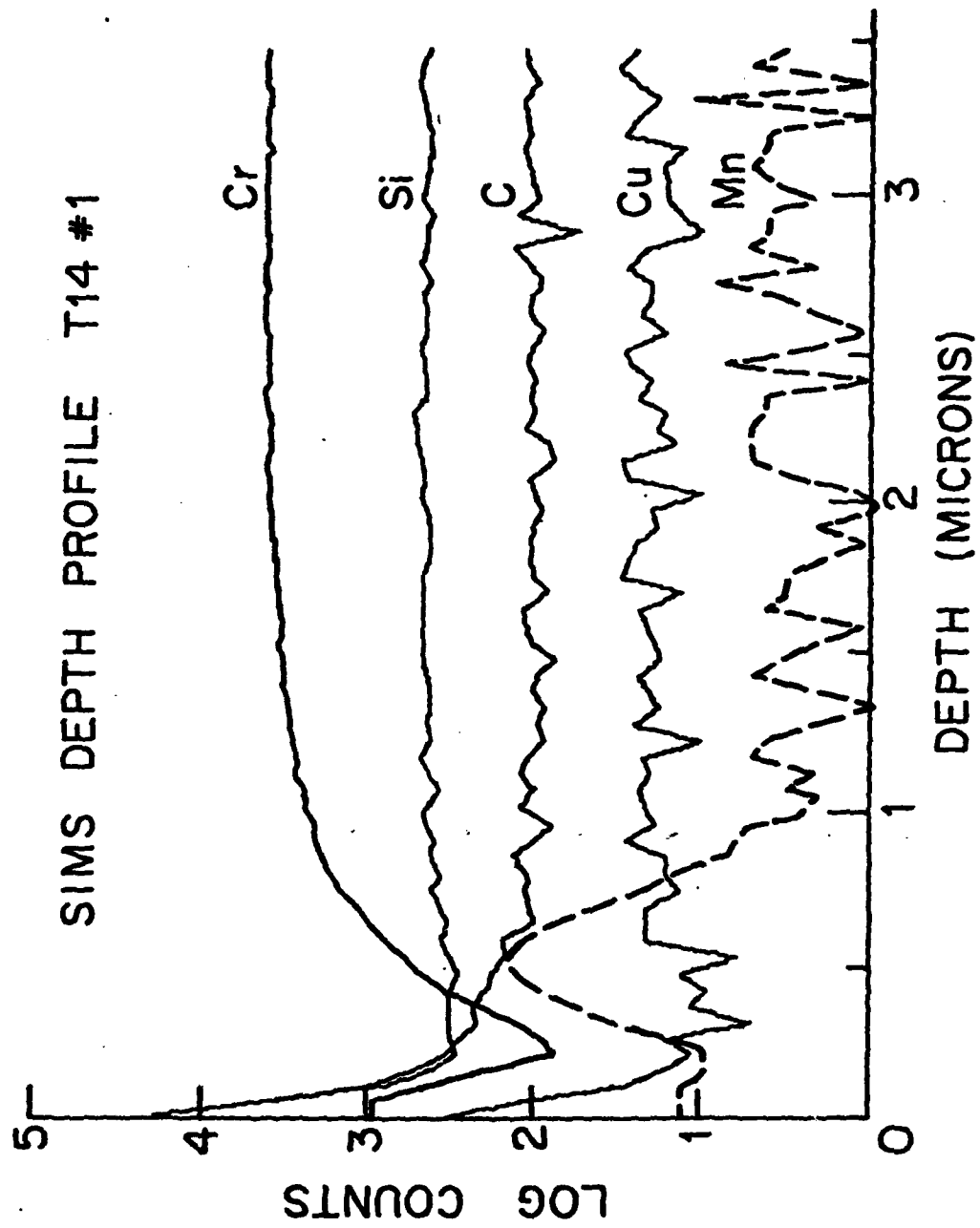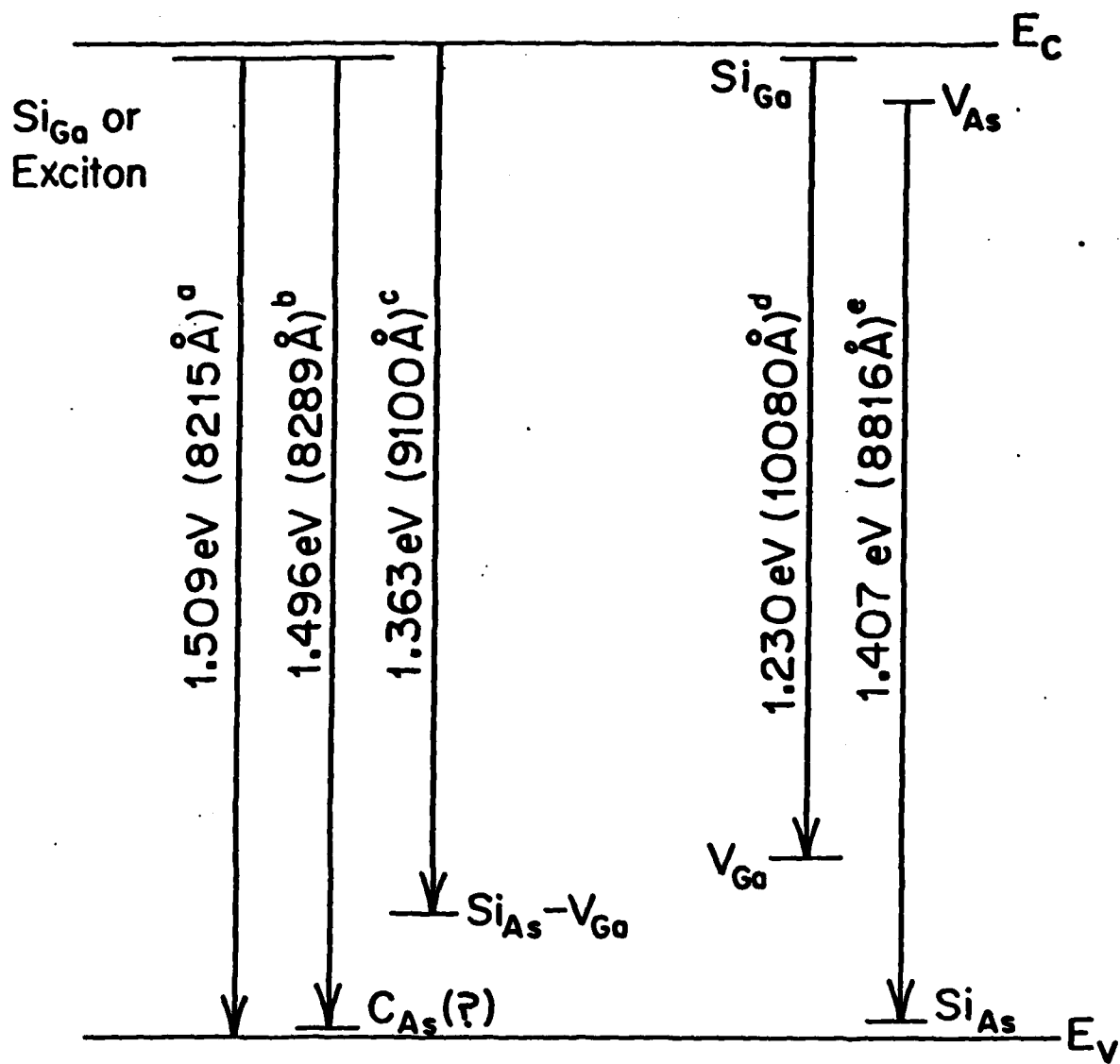Wavelength (Å)

Relative Intensity

8310 Å
9100 Å
8790 Å
8180 Å
8215 Å
8289 Å
8816 Å
9020 Å
9320 Å
9570 Å
9250 Å
x 25

Fig 2

Fig 3

Relative Intensity

Wavelength (Å)

8215 Å

9100 Å

9320 Å

9570 Å

8816 Å

8215 Å

8289 Å

10088 Å

X4000

X25

X2

Fig 4

Fig 5

Fig 6

Fig 7

SIMS DEPTH PROFILE T2 #1

Cr
Si
C
Mn
Cu

DEPT (MICRONS)

LOG COUNTS

Fig 8

SIMS DEPTH PROFILE T10 #1

Cr
Si
C
Cu
Mn

LOG COUNTS

DEPTH (MICRONS)

Fig 9

SIMS DEPTH PROFILE T14 #1

Cr
Si
C
Cu
Mn

LOG COUNTS

DEPTH (MICRONS)

Fig 16

Fig 11

USE OF CATHODOLUMINESCENCE AND SIMS IN THE STUDY OF THERMAL CONVERSION OF SEMI-INSULATING GaAs

S. Y. Yin and D. B. Wittry

Chromium-doped GaAs because of its high resistivity is frequently employed as a substrate for device fabrication. One of the problems encountered in device fabrication with semi-insulating GaAs has been the tendency for thin surface layers of low resistivity to form during heat treatment at temperatures used for epitaxial growth or post ion implantation annealing. In this paper work is described in which cathodoluminescence and SIMS are used to investigate this problem of thermal conversion.

Previous researchers have used a variety of techniques including photoluminescence[1-4] or SIMS[5] because both of these techniques provide high sensitivity for detection of impurity effects in GaAs. However, the results of photoluminescence can be misleading because the excitation depth is small compared to thickness of the thermally converted layers (typically 1-2 microns). With cathodoluminescence, for example at 40 kv the mean carrier generation depth is approximately 2 microns. A comparison of photoemission spectra and cathodoluminescence spectra obtained from the same specimens shows significant differences and some of the strong peaks in the photoluminescence spectra are seen in the cathodoluminescence spectra only when the electron beam voltage is reduced. Thus it seems clear that cathodoluminescence is a preferred method to investigate the mechanisms involved in thermal conversion.

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In this work 14 specimens of GaAs were studied including 6 untreated specimens, 4 specimens heat-treated in hydrogen in a tube furnace and 4 specimens heat-treated by the "Melt Controlled Ambient Technique" (MCAT).[6] The latter technique, developed at Hughes Research laboratories involved immersion of a graphite box containing the specimens in a large melt of gallium saturated with GaAs. The box has a sliding lid which may be opened for growing layers by liquid phase epitaxy but is left closed for heat treatment. In the latter case, the vapor pressure of Ga and As are determined by ambient conditions — hence the term MCAT.

Typical cathodoluminescence spectra at 30°K for a specimen that had a very low resistivity surface layer are shown in Fig. 1. (solid line). This specimen was heat-treated in H_2 at 800°C for 1/2 hour. In the same figure, the dotted line represents the 30°K spectra for a specimen from the same ingot but without heat treatment. The 10,088 Å (1.23 eV) peak has been attributed by Hwang[1] and Williams[7] to recombination involving a Si-donor-Ga-vacancy complex. This peak was observed in all of the specimens examined. The small peak at 8289 Å (1.496 eV) may be due to free electron capture at a shallow neutral acceptor (the acceptor may be carbon on an arsenic site as reported by Lum et al.[2] since the GaAs was supported by a graphite boat during heat-treatment). The peak at 8816 Å (1.407 eV) is presumed to be due to a Si-acceptor-As-vacancy complex previously reported in doped samples of bulk GaAs.[16] The peak at 9100 Å (1.363 eV) is presumed to be due to a Si acceptor-Ga vacancy complex $(Si_{As}\text{-}V_{Ga})$,[9] or a shallow donor (Si_{Ga}) - Cu acceptor (Cu_{Ga}^-)[1] or recombination at Ga vacancies.[10] The two shoulders at 9320 Å (1.33 eV) and 9570 Å (1.296 eV) are LO phonon replicas of the 9100 Å peak.

The 9100 Å (1.363 eV) peak seems to be a key to the mechanism for thermal conversion because it was found by Hall effect measurements of several specimens that the intensity of this peak increased monotonically

with the carrier concentration of the surface layers.

SIMS depth profiles were obtained for 12 of the specimens studied
by cathodoluminescence. The secondary ion intensities of Cr, Si, C, Mn and Cu
for the heat-treated specimen of Fig. 1 are shown in Fig. 2. The Cu ion
intensity obtained from this specimen is not significantly higher than
obtained from other specimens examined. The Si ion intensity is also not
unusually high but the heat treatment conditions for this specimen are
expected to produce a high As and Ga vacancy concentration. Thus the
principle mechanism for thermal conversion of semi-insulating GaAs may be
a Si_{As}-V_{Ga} complex formed during heat treatment. Obviously there are other
possible interpretations, for example the depletion in Cr in the converted
layer may lower the resistivity--but this cannot account for the increase
in the intensity of the 9100 $\mathring{A}$ peak.

A more detailed description of this work and analysis of the results
is being submitted for publication elsewhere.

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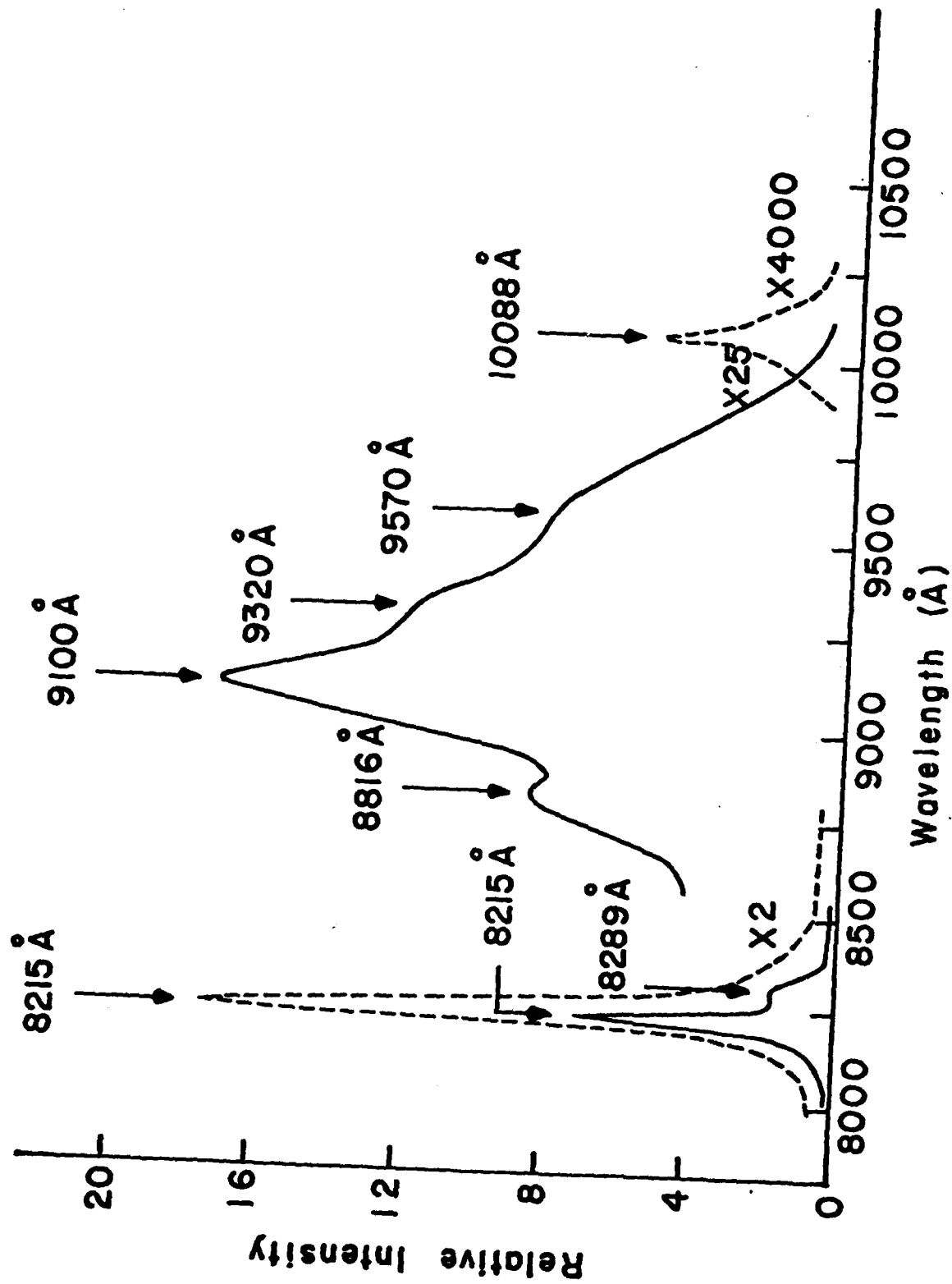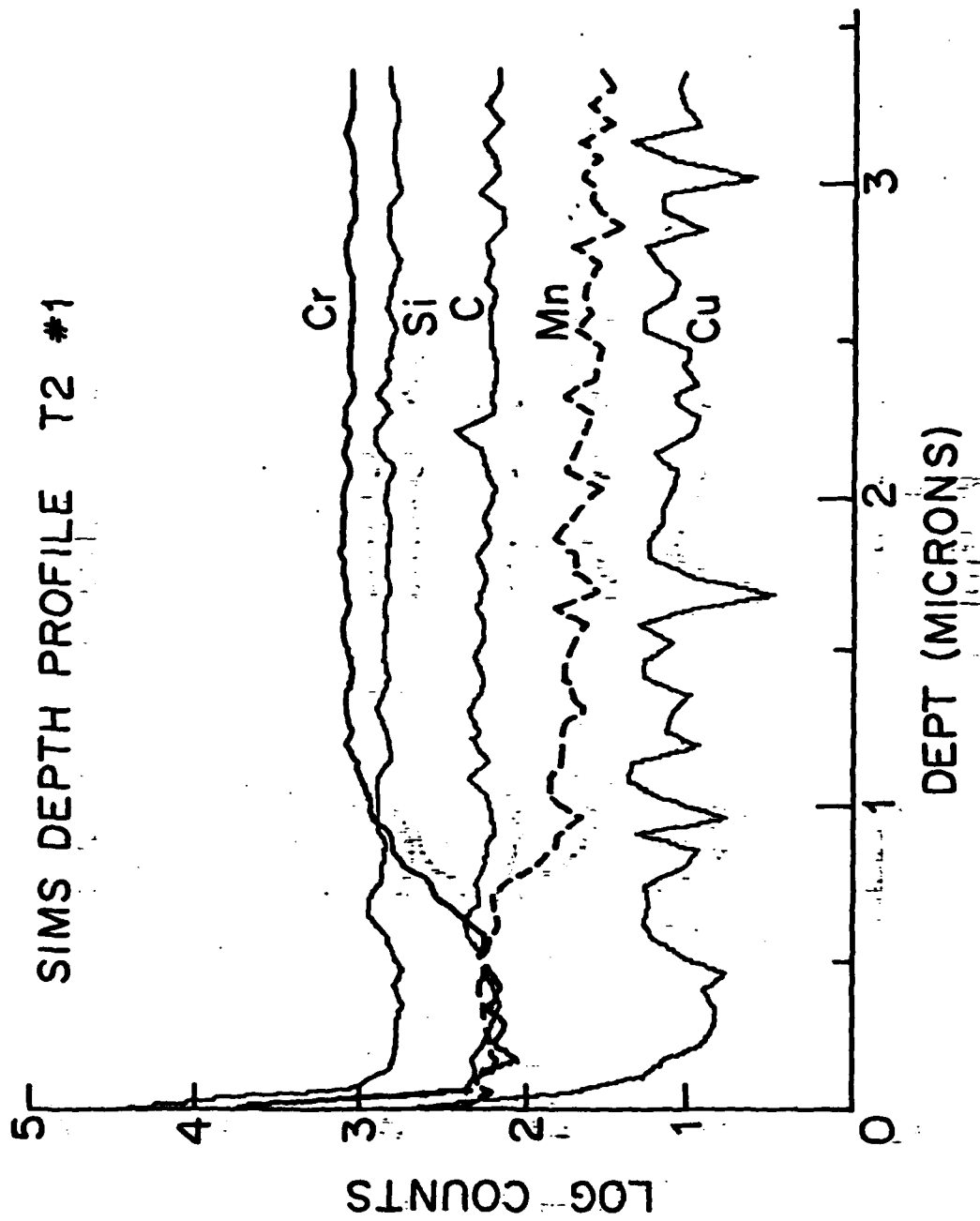
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Fig. 1

Relative Intensity

Wavelength (Å)

8215 Å
8215 Å
8289 Å
8816 Å
9100 Å
9320 Å
9570 Å
10088 Å

X2
X25
X4000

SIMS DEPTH PROFILE T2 #1

Cr
Si
C
Mn
Cu

DEPT (MICRONS)

LOG COUNTS

Fig 2

DATE
FILMED

8